Graduated Center Projects

- **Major Accomplishments**

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C S P

Graduated Project
Design and Synthesis of Ultrahigh-Temperature Intermetallics

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Generate the knowledge required to establish a scientific basis for the design and processing of transition-metal silicides and materials based on silicides for structural applications at temperatures of 1400°C and above.*

Tasks

- First Principles Calculations/Simulations
- Structure and Properties
- Processing and Fabrication

Focus: Mo_5Si_3-base Alloys

Participants

- Ames, ANL, INEEL, LBNL, LLNL, LANL, ORNL, SNL/CA, UI/MRL

Coordinators

- R. Judkins, ORNL, (423) 574-4572/judkinsrr@ornl.gov, R. B. Thompson, Ames (515) 294-8152 thompsonrb@cnde.iastate.edu

Sponsoring/Collaborating Organizations

BES/DMS&E **FE/AR&TD** **EE/AIM**

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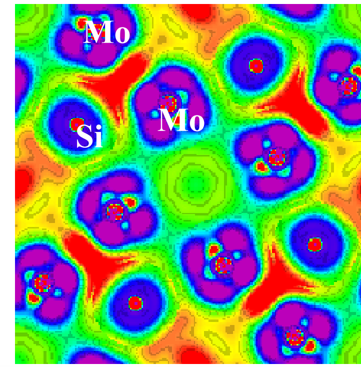
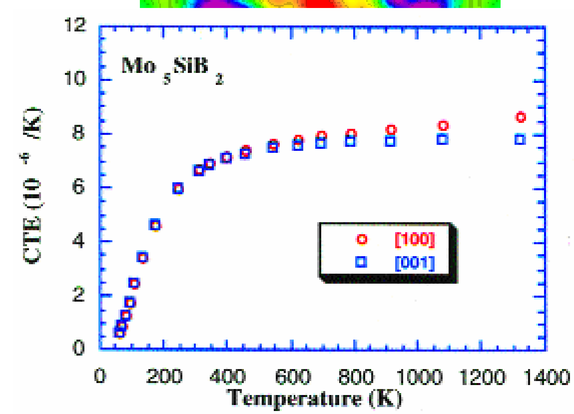
Graduated Project
Design and Synthesis of Ultrahigh-Temperature Intermetallics

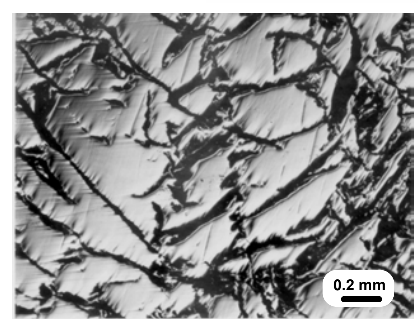
Basic Energy Sciences
Division of Materials Sciences and Engineering

Major Accomplishments

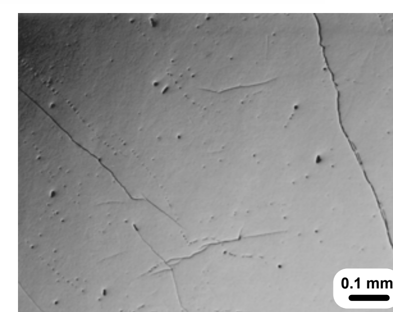
- First-principles calculations established the nature of the bonding in Mo_5Si_3 and revealed the influence of alloying (B, Al) on phase behavior, thermal expansion anistropy and elastic properties.
- Alloying results agree with calculations
  - Al retains T1 phase; large CTE anistropy; grain boundary cracking
  - B $\rightarrow T_2$ phase; 30% higher hardness and fracture toughness; reduced CTE anistropy; greatly reduced cracking; improved processing
  - Nb and V reduce CTE







Mo_5Si_3



$(Mo_{0.4}Nb_{0.6})_5Si_3$

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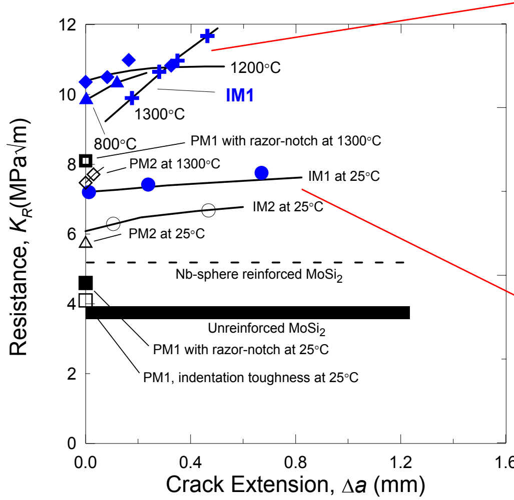
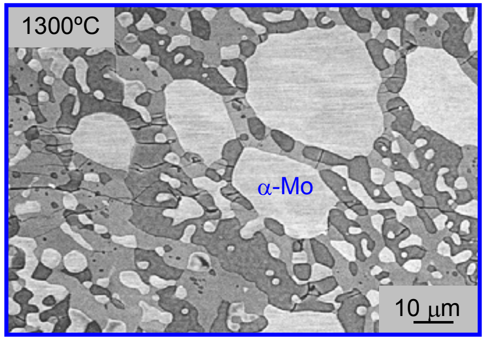
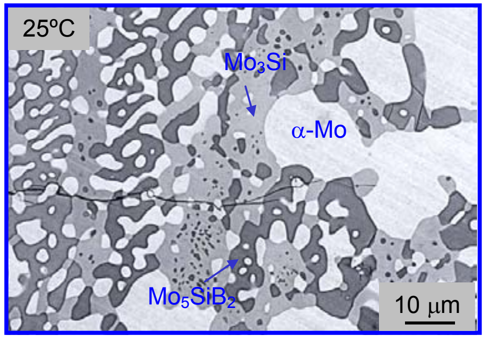
Major Accomplishments (Cont'd)







- A process to improve the fracture toughness of Mo-Si-B alloys was developed and demonstrated. The process is based on the consolidation of Mo-coated Mo-Si-B particles leading to the formation of Mo_3Si and Mo_5SiB_2 phases in a continuous α-Mo matrix.

- Showed that the boron-modified molybdenum silicide alloy, Mo-12Si-8.5B (at.%), can be processed to be considerably tougher and more fatigue resistant than both monolithic $MoSi_2$ and Nb-sphere reinforced $MoSi_2$. Additionally, the crack-growth resistance of this B-modified alloy increases progressively with increasing temperature up to 1300°C.

Major Accomplishments (Cont'd)

- Stress-strain properties and dislocation structure studies on T2 Mo-Si-B alloys produced by powder metallurgy exhibit high plasticity above 1400°C as well as high strength (140 MPa at 10^{-4}/s).
- The high temperature strength of Mo-Si-B alloys was shown to depend strongly on the topology and scale of the alloy's microstructure. For comparable compositions, the creep strength can be varied by as much as a factor of two by manipulating the microstructure and its scale.
- Showed that a protective scale forms on Mo-Si-B alloys during isothermal oxidation that significantly reduces oxygen transport and the formation of Mo and MoO2 precipitates at the scale/alloy interface. These borosilicate scales as well as sulfide scales formed during sulfidation experiments may greatly improve oxidation and corrosion resistance.

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Graduated Project

High Efficiency Photovoltaics

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Generate advances in scientific understanding that will impact the efficiency, cost and reliability of thin film photovoltaics cells by addressing the short- and long-term basic research issues.*

Tasks

- Silicon-Based Thin Films
- Next-Generation Thin Film Photovoltaics:

  Focus: Multijunction cell with ≥ 40% efficiency

Participants

- Ames, ANL, BNL, LBNL, NREL, ORNL, PNNL, SNL/NM, SNL/CA, Caltech, Iowa State U., U. of Calif. (Santa Barbara), MIT, U. of IL, U. of FL, Wash. St. U., SUNY Buffalo, U. of UT

Coordinators

- Satyen K. Deb/J. Benner, NREL, (303) 384-6405, satyen_deb@nrel.gov

Sponsoring/Collaborating Organizations

BES/DMS | EE/Photovoltaics | EPRI

CSP

Graduated Project

High Efficiency Photovoltaic

Basic Energy Sciences
Division of Materials Sciences and Engineering

Major Accomplishments

- A new model for light-induced metastability in hydrogenated amorphous silicon (a-Si:H), the so-called Staebler-Wronski effect responsible for the degradation of a-Si:H solar cells, was developed. Molecular dynamic simulations have revealed several atomic configurations that satisfy the model.
- Positron annihilation provided the first identification of the negatively charged Si dangling bond/Phosphorous complex defect in a-Si:H. Should lead to a better understanding and control of the structure electronic properties of a-Si:H.
- Hot-Wire Chemical Vapor Deposition (HWCVD) combined with post-deposition metal-induced crystallization was shown to produce Si films with 0.1µm grains suggesting that this approach may be viable for producing thin Si film solar cells. The fast growth rates and low-temperature processing involved are attractive aspects of this approach.
- An optically-assisted, low-temperature process for enhancing the grain size of thin Si film has been developed. A device structure employing such films has the potential for producing high-efficiency (~18%), low-cost solar cells.
- Defined a major challenge: A 4-junction solar cell with conversion efficiency > 40%. Identified a 1eV bandgap GaInNAs alloy as the key to its implementation.
- Much progress made towards understanding the origin of the relatively low electron lifetime, mobility and diffusion length in GaAsN and GaInAsN and a model consistent with the results was developed.

Major Accomplishments (cont'd.)

- Advanced diagnostics led to deep insight into the physics
  - Synchrotron radiation allowed a non-destructive and element-specific means for determining interfacial roughness, correlation lengths of thickness fluctuations, elemental density profiles and the local environment of specific atoms in heterojunction solar cells.
  - A resonance acoustic technique was developed that has the potential for providing on-line quality control of Si wafers at different processing steps.
  - Synchrontron x-ray fluorescence identified metal impurities and their chemical states in poly Si and correlated with cell performance. Fe likely responsible for poor performance.

- Theory led to deep insight into the physics
  - Density functional theory led to understanding of: defects and their interactions with dopants; diffusion of dopants; relaxation of defects; reconstruction energies; dislocations; amorphous-crystal interface; solid state epitaxy; and routes to large-grain poly Si.

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Graduated Project

Interfacial Adhesion Related to Protective Oxides Grown on Metallic Substrates

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Further the fundamental understanding of the interfacial bonding and dynamics that underlie oxide-metal adhesion and the energetics associated with decohesion for systems relying on protective alumina through theoretical calculations, experimentation and modeling.*

Tasks

- Nature of bonding at oxide interfaces and the effects of segregants
- Stress measurements, microstructure and modeling of diffusion-induced stress generation
- Modeling of pore formation and interaction

Participants

- ANL, INEEL, LBNL, ORNL

Coordinator

- Linda Horton/PeterTortorelli, ORNL (423) 574-5081, hortonll@ornl.gov

Sponsoring/Collaborating Organizations

BES/DMS&E FE/ATS Westinghouse, Pratt & Whitney, Allison Engines

Graduated Project

Interfacial Adhesion Related to Protective Oxides Grown on Metallic Substrates

Basic Energy Sciences
Division of Materials Sciences and Engineering

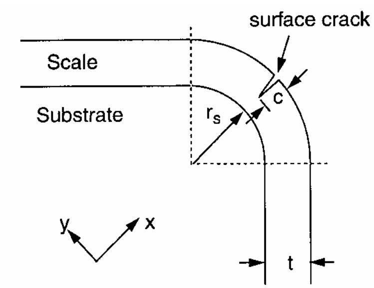
Follow-on to “Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance”

Objectives:

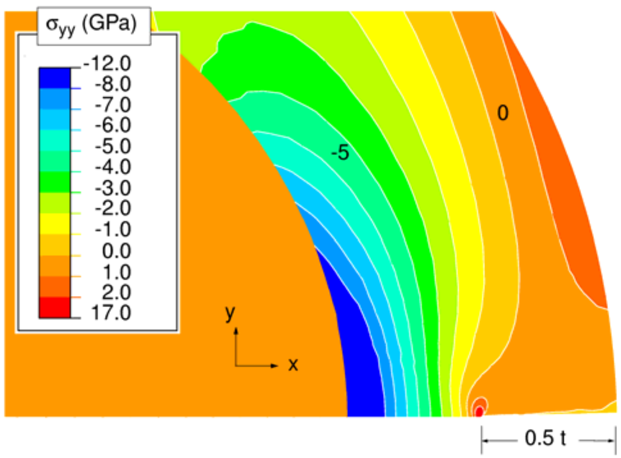
- **Generate the knowledge required to establish a scientific basis for the design and synthesis of adherent protective oxide coatings and scales on high temperature materials without compromising the requisite material properties.**
- **Understand the interfacial bonding and dynamics that underlie oxide-metal adhesion as well as the energetics of decohesion.**

Focus:

- **Alumina coatings on Fe-Al-Cr modeling**
- **Combined experiments, theory and modeling**



Schematic of surface crack at corner



Contour plot of S_{yy} in the vicinity of a surface crack through half the scale thickness

Graduated Project

Interfacial Adhesion Related to Protective Oxides Grown on Metallic Substrates

Basic Energy Sciences
Division of Materials Sciences and Engineering

Major Accomplishments

- Demonstrated that plasma-deposited alumina coatings can provide excellent high temperature oxidation protection to Fe-Al-Cr alloys. Adhesion of the alumina is further enhanced by the presence of Zr in the alloy.
- Auger electron spectroscopy revealed elevated levels of S at the oxide-metal interface in thermally-grown alumina on a Fe-Al-Cr alloys leading to poor scale adhesion. With 0.1 at.% Zr in the alloy, no sulfur was observed at the interface and there is good scale adhesion – an alloying route to reliable coatings.
- Determined that the high temperature segregation of S to the oxide/metal interface is controlled by the availability of binding sites and not bulk diffusion.
- Advanced tools (e.g., synchrotrons and positron annihilation) were   used to characterize and understand the role of vacancies, vacany clusters and strain during oxide growth.
- In-situ ruby fluorescence and finite element modeling were combined to provide a detailed view of stress gradients and failure locations during growth as well as during temperature cycling. Led to an improved understanding of failure mechanisms and local fracture behavior.

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Graduated Project

Materials Joining

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Improve the reliability of the processes used to join materials into more complex structures serving a variety of energy-related functions.*

Tasks

- The Effects of Gradients on Weld Reliability and Performance *Focus: Al-Cu and Fe-Ni-Cr Alloys*
- Ceramic and Dissimilar Materials Joining *Focus: Joining SiC and SiC-based CFCCs*

Participants

- Ames, INEEL, LBNL, LLNL, ORNL, PNNL, SNL/CA, SNL/NM

Coordinator

- R. Bruce Thompson, Ames, (515) 294-8152

Sponsoring/Collaborating Organizations

BES/DMS	FE/AR	EE/OTT	EE/OIT	DP

Major Accomplishments

Ceramic Joining

- Development and maturation of 4 technologies
  - Transient liquid phase joining
  - Air-fired polymer-precursor SiC joining
  - Solid state displacement reaction joining
  - Reaction bonding

- Two Symposia held at American Ceramic Society meetings

- Strong links forged between BES researchers and FE/CFCC staff and industrial partners

Major Accomplishments (Cont'd.)

Influence of Gradients on Weld Reliability and Performance

- New understanding and modeling of weld solidification and phase microsegregation
- First in-situ video camera studies of weld pool dynamics, instabilities and solidification including influence of welding speed
- First real-time studies of the evolution of phase transformations during welding and solidification using SRXRD and TRXRD
- Neutron diffraction provided accurate measures of residual stresses in welds
- Degradation in weld properties in stainless steels related to phase transformation during aging. Remedy: alloy modification
- Predictive thermo/kinetic model for the formation of non-metallic inclusions during welding developed
- Strong interactions with welding community: Welding Institute, Am. Welding Soc., Lincoln Electric

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Graduated Project

Tailored Microstructures in Hard Magnets

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Improve hard magnets by understanding, in terms of the microstructures achieved, the magnetic and mechanical properties of materials produced by a number of synthesis and processing approaches.*

Tasks

- Synthesis: Powders, Compacts, Single Crystals, Thin Films.
- Characterization: Magnetic and Structural Properties.
- Theory and Modeling

Focus: $Nd_2Fe_{14}B$ as a Model System; Novel SmCo-based Systems

Participants

- Ames, ANL, BNL, INEEL, LBNL, LLNL, LANL, ORNL

Coordinator

- Robert Dunlap, ANL, (630) 252-4925

Sponsoring/Collaborating Organizations

BES/DMS EE/OTT DP Consortium for Advanced Magnets (university/industry)

Graduated Project

Tailored Microstructures in Hard Magnets

Major Accomplishments

Developed a high level mastery of the role of microstructure in hard magnets

- Developed detailed understanding of the microstructure of Nd-Fe-B magnets and synthesis and processing approaches to produce homogeneous microstructures for optimum magnetic properties

- Developed synthesis and processing approaches to improve the properties of nanocomposite magnets and applied to Pr-Co magnets for high temperature applications

- Demonstrated the concept of *Exchange Spring Magnets* to creat thin film permanent magnets with enhanced strength based on combining known materials in new nano-configurations (e.g., Sm-Co/Fe, Co)

- Strong ties to/interactions with the magnetics community

CSP

Graduated Project

Processing for Surface Hardness

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Address the critical synthesis and processing issues which limit the use of plasma-based processing for improved surface hardness. Explore other novel approaches for achieving the same.*

Tasks

- Plasma Ion Immersion Processing (PIIP)
- Boron-Based Superhard Coatings: *Focus: cBN, Boron Suboxides*
- Tailored Microstructures for Tribological Applications:

  Focus: Diamond Films, Al/O, Nanoscale Structures

Participants

- ANL, BNL, LBNL, LLNL, LANL, ORNL, SNL/CA, SNL/NM, UI/MRL

Coordinator

- James B. Roberto, ORNL, (423) 576-0227

Sponsoring/Collaborating Organizations

BES/DMS **EE/OTT** **DP**

Graduated Project

Processing for Surface Hardness

Basic Energy Sciences
Division of Materials Sciences and Engineering

Major Accomplishments

Novel Synthesis and Processing approaches led to the formation of hard films with unique/unusual properties

- **Carbon Films**
  - **Alternating soft/hard multilayers with wear rates 10-1000x less than other hard coatings**
  - **Diamond-like C coatings on Ni yielded dramatic improvements in friction and wear properties; applied to MEMS gears**
  - **Smooth, ultrananocrystalline (3-5 nm) diamond films up to 30+ μm thick successfully grown by plasma-assisted CVD. Exceptional wear on rotary shaft pump seals**

- **Boron-based Films**
  - **Amorphous boron suboxide with hardness (H) = 30 Gpa (≡ 15X that of mild steels**
  - **Substrate voltage bias led to smooth boron carbide films (H = 40 Gpa)**
  - **N^+ implantation of as deposited hBN films → cBN w/o loss of adhesion; produced B films with H = 40 GPa**

2-D and 3-D Finite Element Modeling and nano-indentation quantified intrinsic properties of hard films on soft substrates

Micromachined Si cantilever beam measured stress during film growth

Interactions with DP and EERE programs and with industry

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Graduated Project

Mechanically Reliable Surface Oxides for High-Temperature Corrosion Resistance

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Generate the knowledge required to establish a scientific basis for the design and synthesis of improved (slow growing, adherent, sound) protective oxide coatings and scales on high temperature materials without compromising the requisite bulk material properties.*

Tasks

- Substrate/Protective Oxide Interactions.
- Prediction of Scale/Coating Failure.
- Requirements for Improved Scales/Coatings.

Focus: Alumina Scales and Coatings

Participants

- ANL, INEEL, LBNL, LLNL, ORNL

Coordinator

- Linda L. Horton, ORNL, (423) 574-5081

Sponsoring/Collaborating Organizations

BES/DMS **FE/AR** **EPRI**

Graduated Project

MRSOX

Major Accomplishments

- Advanced Analytical tools (XRF, Auger, Raman, TEM, STM, positrons) have provided unprecedented insights into the chemistry, composition, roughness, and defect structures of Al_2O_3 films and underlying substrates and led to new strategies for the growth of dense adherent films
- Understanding of the mechanisms of S segregation to the metal/Al_2O_3 interface, the role of S in interfacial debonding and new approaches to improve scale adhesion
- Better understanding of stress distributions in oxide layers yielded insights into appropriate measurement and modeling approaches and into how strain accumulation contributes to the energetics of film decohesion
- Strong interactions with EERE and FE programs (joint funding) and with the scientific community

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Graduated Project

Microstructural Engineering with Polymers

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Develop and implement novel processing methods which direct the evolution of hierarchical microstructures in composites, impart multifunctionality, and induce property changes through blending of components at the molecular level.*

Tasks

- Engineered Porosity

  *Focus: *Surfactant-Templated Ceramic Phases*
  **Inorganic Polymer Membranes*

- Blends, Composites, Alloys

  *Focus: *Conducting Polymers*
  **Polymer Molecular Composites*
  **Polymer Blend Miscibility*

Participants

- Ames, ANL, BNL, INEEL, UI/MRL, LBNL, LLNL, ORNL, PNNL, SNL/NM

Coordinator

- Gregory J. Exarhos, PNNL, (509) 375-2440

Sponsoring/Collaborating Organizations

BES/DMS EE/OIT EE/OTT Armstrong World Ind. Advanced Battery Consortium
Power Conversion Inc. Gould Electronics Technochem, Inc. Hoechst-Celanese

Graduated Project

Microstructural Engineering with Polymers

Basic Energy Sciences
Division of Materials Sciences and Engineering

Major Accomplishments

- A new class of molecularly-tailored ceramic composites were developed. Self-Assembled Monolayers on Mesoporous Supports (SAMMS) integrates mesoporous ceramics technology with an innovative method involving chemical attachment of specific molecules to an oxide surface which can selectively bind a wide range of metal contaminants.

- Optimum processing conditions were found for producing carbon aerogels with tailorable pore morphology and targeted properties. New polymeric compositions can be produced using simple drying protocols that do not require complex processing and supercritical fluid drying.

- Two new routes for the synthesis of inorganic and molecularly mixed inorganic-organic polyphosphazene 3-D membranes and porous films were developed. Potential applications in the fuels industry and environmental cleanup.

- A new family of stable anion complexing agents based on either cyclic, linear or branched amines containing electron withdrawing side groups was developed. These compounds increase the transport number of Li+ ions, a key to improving the performance of Li batteries.

- Using the off-lattice Polymer Reference Interaction Site Model (PRISM), it was demonstrated that the structural parameters (bond lengths, bond angles, torsion angles, and halogen separations in both the gauche and trans conformations) of small monemeric analogues accurately determine the packing architecture of saturated hydrocarbon polymers.

- Solid state NMR methods were used to probe the local chemical environment inside ordered nanochannels to enable protocols for the structural manipulation of polymer-derived nanocomposites. Shear and magnetic field alignment have been shown to extend the intrinsic small-scale order to the macroscopic scale.

C S P

Graduated Project

Metal Forming

Basic Energy Sciences
Division of Materials Sciences and Engineering

Objectives

- *Develop a scientific understanding of the phenomena relating to the forming of aluminum alloys for industrial (especially automotive) applications.*

Tasks

- Dynamics of Dislocation Substructure
- Particle-Stimulated Recrystallization
- Constitutive Equations for Hot Rolling

Focus: Al-Mg and Al-Cu Alloys

Participants

- Ames, LBNL, LLNL, LANL, ORNL, PNNL, SNL/CA, SNL/NM, UI/MRL, Cornell, Oregon State

Coordinator

- Michael Kassner, Oregon State, (541) 737-7023

Sponsoring/Collaborating Organizations

BES/DMS	**EE/OTT**	**DP**	**Alcan**	**Reynolds Aluminum**

Graduated Project

Metal Forming

Major Accomplishments

- Although the complexity of microstructures resulting from metal forming processes had appeared to defy any quantitative interpretation, we discovered scaling relationships indicating that universal laws govern the evolution of the dislocation structure and resulting grain refinement during large strain plastic deformation. TEM observations on fcc metals/alloys support this finding. Important for improving formability.

- By manipulating the microstructure through an understanding of the role of precipitates in the recrystallization process, we demonstrated high superplasticity (deformation up to 600% at a strain rate of $1x10^{-4}s^{-1}$ and >300% even at $1x10^{-2}s^{-1}$) in a relatively low cost Al-Mg alloy similar to the commercial 5083 alloy.

- Studies of the superplastic alloy Al-6Mg-0.3Sc led to better understanding of the role of fine Al_3Sc particle precipitates in the recrystallization and deformation behavior of this alloy and to the ability to tailor its mechanical properties.

- We demonstrated that semi-solids can be produced exclusively by thermal treatments, providing a novel and inexpensive alternative to conventional Al casting.

- We showed that the slip on the (011) octahedral planes is responsible for the bimodal texture observed in the high temperature forming of Al alloy 5182.

- An ultrasonic technique sensitive to differences in bulk rolling and recrystallization textures of Al was developed. Key advantages over other approaches (e.g., X-ray measurements) are that it provides a volume (not near surface) average of the texture and is compatible with the manufacturing environment.